

In Situ UV-Visible Spectroelectrochemical Studies on Electrochromic Behavior of Poly(2,5-dimethoxyaniline)

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Introduction

Polyaniline retains extensive interest because of the technological applications such as electrode for display devices, sensors, electrocatalysis and rechargeable batteries. Among the potential applications, the use of PANI in "electronic device" has attracted considerable interest owing to the possible utility in microelectronics [1]. Electrochromic display devices or "smart windows" have been greatly studied [2]. The use of these devices in buildings can decrease the energy consumed by heating and illumination. Therefore, electrochromic devices and "smart windows" are frequently proposed as the most promising applications for PANI and related conducting polymers or its derivatives. However, many problems are to be solved for useful applications of PANI in electrochromic systems. A relatively slow response of PANI to an electrochemical perturbation should be considered as one of them.

Aniline substituted with two methoxy groups, 2,5-dimethoxy aniline (DMA), has been reported to produce soluble polymer, poly(2,5-dimethoxy aniline), PDMA with a conductivity similar to polyaniline.

Bernard and Hugot Le Goff [3] used an optical multichannel analysis (OMA) to follow the kinetics of color changes in PANI films during electrochemical conversion and found that these changes occurred very fast and allow one to estimate the practical possibility of using PANI in electrochromic devices. This prompted us to study the electrochemical, optical and spectroelectrochemical properties of PDMA in a systematic way and explore the possibility of using this polymer as electrochromic material.

Results and Discussion

Fig. 1 represents the CV of the PDMA film in 0.5 M H_2SO_4 . The PDMA film was deposited by reversibly cycling the potential in the range of 0.0 V to 1.0 V vs. Ag/AgCl on a solution of DMA (10 mM) in 0.5 M H_2SO_4 . Two well separated redox peaks at (0.17 V/ 0.11 V) (A/A') and (0.27 V/ 0.20 V) (B/B') along with a weak anodic shoulder at 0.38 V were observed. The first two redox peaks are attributed to conversion of leucoemeraldine to emeraldine and emeraldine to pernigraniline transitions. Interestingly, the appearance of a very weak shoulder at 0.38 V indicates the minimum or negligible incorporation of oligomers or degradation products of polymer in the selected experimental conditions.

Electrochromic properties of PDMA were studied by spectrochronoamperometry. We have studied the effect of potential step (between 0.0 V to 0.4 V wherein PDMA showed transitions between oxidized and reduced states) on the optical response of PDMA by following the spectrochronoamperometric results. Fig. 2 exemplifies the results of the experiment for PDMA film showing the electrochemical response (current density vs. time, Fig. 2,

plot b) and optical response (absorbance vs. time at $\lambda = 770$ nm, Fig. 2, plot a). The time necessary for complete coloring of the film was found to be 9 sec. This time is much smaller than for the electrochemically prepared PANI film (22 sec). Hence, rate of coloration can be considered to influence by the ease of oxidation (0.4 V) to its maximum state than affected by the conformational variations due to the presence of bulky methoxy groups present in PDMA films.

References

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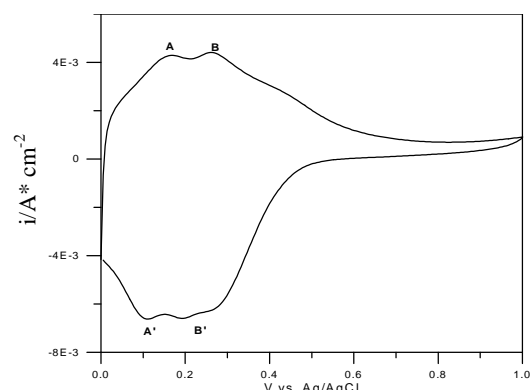


Fig. 1. Cyclic voltammogram of PDMA-modified Pt electrode in 0.5 M H_2SO_4 .

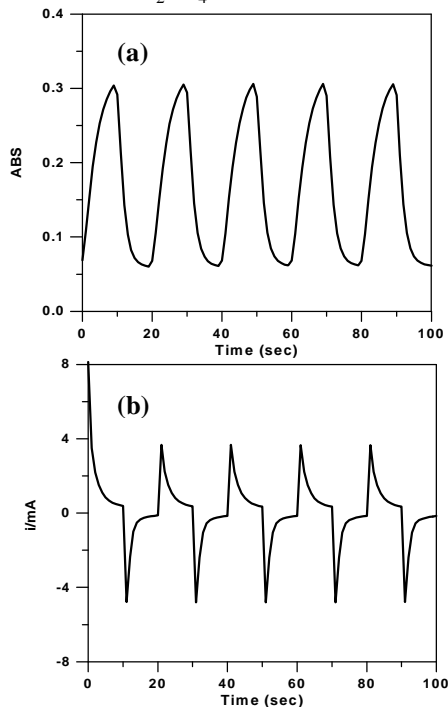


Fig. 2. Absorbance-time (a) and current-time (b) profiles of PDMA recorded during double step spectrochronoamperometry.